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STUDY OF O_2 REDUCTION ON SILVER-LEAD MIXTURES FORMED BY ATOMIC SPUTTERING

Report No 90-16-K

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ABSTRACT

The electroreduction of oxygen in alkaline media has been studied on atomically sputtered silver films and cosputtered silver-lead mixtures over a wide range of composition. The results of a comparative study reveal that several silver-lead mixtures display reproducible and significantly better kinetics for O_2 reduction than pure sputtered silver films up to a surface metal ratio of Pb/Ag 2.4. Characterization by Auger, XPS and XRD spectroscopies reveal the films to be non-uniform and the surface coated with an oxide layer. The voltammetry behaviour of these metal mixtures is not simply a superposition of the individual metal components at high lead concentrations, suggesting a modification of the silver-silver oxide redox system. The accompanying improvement in O_2 reduction kinetics suggests that there exists a correlation between this modified redox behaviour of the silver/silver oxide system and the former improvement.

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EXECUTIVE SUMMARY

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The fabrication and screening of new O_2 cathode materials based on binary mixed metals and metal oxides employing silver is motivated by several properties of silver which are conducive to efficient O_2 reduction. These properties can potentially be enhanced synergistically by mixing with other components. The choice of lead as the alternate metal component is motivated in part by the fact that underdeposited lead on platinum and gold results in substantially increased O_2 reduction kinetics. Surface alloy formation of lead with the underlying substrate is one possible explanation and hence we are extending this principle to forming mixed metal structures. In addition, various oxides of lead are known to be highly efficient peroxide decomposition catalysts. Coupling with silver which is also an excellent decomposition catalyst may be expected to result in a better peroxide decomposition catalyst.

The electroreduction of oxygen in alkaline media has been studied on atomically sputtered silver films and cosputtered silver-lead mixtures over a wide range of composition. The results of a comparative study reveal the silver-lead mixtures display reproducible and significantly better kinetics for O_2 reduction than pure sputtered silver films up to a surface metal ratio of Pb/Ag 2.4. Characterization by Auger, XPS and XRD spectroscopies reveal the films to be non uniform and the surface coated with an oxide layer. The voltammetry behaviour of these metal mixtures is not simply a superposition of the individual metal components at

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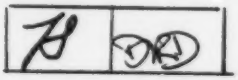

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To Dr. D. Mills
Director of Research

STUDY OF O_2 REDUCTION ON SILVER-LEAD MIXTURES FORMED BY ATOMIC SPUTTERING

1.0 INTRODUCTION

Silver, along with the noble metals platinum and gold remains one of the better O_2 reduction electrocatalysts. That silver is ≈ 60 times cheaper than either platinum (or gold) and ≈ 10 times more abundant (1) makes it a serious alternative to the latter two as a viable O_2 reduction electrocatalyst in both energy conservation and generation applications. Oxygen electroreduction on silver has been shown to follow the parallel mechanism or pathway, where both the two electron reduction to peroxide and the four electron reduction directly to water occur (2, 3). The impetus for screening and studying alloys and/or metal mixtures of with silver as one of the components as oxygen reduction catalysts is that several known chemical and electrochemical properties of Ag render it a promising choice. The existence of evidence of the dissociative adsorption of O_2 on silver (4) and the fact that silver has been identified as a good peroxide decomposition catalyst (5) suggest its utility as an oxygen reduction catalyst. Furthermore, in alkaline media silver has associated with it the metal/metal oxide redox couple Ag/Ag_2O (E_o = 0.345 V(NHE)) which is in the vicinity of the reversible O_2/OH^- potential (E_o = 0.401 V(NHE)), a feature which has been linked to the success of other oxygen reduction catalysts. The interpretation of this fact is that chemical oxidation of the metal by O_2 and subsequent electrochemical reduction of the metal oxide amounts to electroreduction of the O_2 molecules. However, the presence of an Ag_2O film which is thermodynamically stable at potentials up to 100 mV negative of the O_2 reversible potential suggests that true reversible behaviour for O_2 reduction by the above mechanism (which calls for essentially an unstable oxide in this region cannot be achieved with silver alone. The presence of this oxide and possibly different suboxides on silver explains in part the strong dependence of O_2 reduction kinetics on electrode potentiostatic and galvanostatic pretreatment (6-8).

Synergistic effects have been reported in which the catalytic activity of certain platinum based alloys exceed the catalytic behaviour of the individual components. These effects, which generally vary in a complex fashion with composition, are not as

yet theoretically predictable. Previous studies of O_2 reduction on silver-magnesium alloys showed that the best results were achieved with the composition, Ag-1.7% Mg (by weight), in which steady state galvanostatic Tafel plots exhibited lower activation overpotentials compared to pure silver while silver alloyed with barium, thorium and indium exhibited no improvement over pure silver (9). In this work we are initiating a series of studies of O_2 electroreduction on mixed metal and mixed metal oxides containing silver as one of the components in the reasonable belief that some of these mixtures will exhibit a greater efficacy for O_2 reduction than pure silver. Atomic sputter deposition, which is being employed as the film fabrication method, will allow the fabrication of mixtures which are mixed on an atomic level and being a non equilibrium growth method will allow stable mixtures to be formed not a ievable by more conventional growth techniques.

2. EXPERIMENTAL

A Perkin-Elmer Model 2400 rf diode sputtering system was used to fabricate the films. Pure silver was sputter deposited from a 6" diameter silver metal target (MRC - 99.9% purity) onto stainless steel discs (area = 0.196 cm^2) which form part of a demountable rotating ring disc assembly (Pine Instruments). Similarly, lead was sputter deposited from a 6" diameter lead metal target (MRC 99.99% purity). Silver oxide, ≈ 1000 Å in thickness was sputter deposited by reactive sputtering in a 100% O_2 plasma at a chamber pressure of 10 microns onto substrates heated to ≈ 150 C. Silver-lead mixtures were formed by cosputtering from the silver and lead targets simultaneously onto the disc electrodes and pyrex flats which were continuously rotated under the targets. The sputtering gas was argon at a chamber pressure of ≈ 10 microns. Auger depth profile studies were performed using a JAMP-10 Auger scanning spectrometer. Cyclic voltammetric (CV) studies and low current density galvanostatic polarization plots were obtained with a Princeton Applied Research (PAR) Model 170 Electrochemistry System. The rotating ring disc studies were carried out using a Pine Instruments rotating ring disc assembly and an EG&G Model 370 Electrochemistry System. Electrochemical studies were carried out in both 1.00 or 0.10 M KOH and NaOH (analytical reagent grade) with the water purified using a Zenopure laboratory Water system Ultra 70 ASPM type grade water. The reference electrode was either the SCE or the Hg/HgO system. A large platinum counter electrode was employed in the cyclic voltammetry studies and a high purity spectroscopic grade carbon rod was used as the counter electrode in the O_2 reduction studies.

3. RESULTS AND DISCUSSION

The cyclic voltammogram of Fig. 1 is for a pure sputtered silver film in nitrogen saturated 0.10 M NaOH. The rotating disc currents

at different rotation speeds for pure silver are shown in Fig. 2 with the linear Levitch-Koutechy plot of Figure 3 showing that the O_2 reduction reaction is first order with respect to dissolved oxygen. Figures 4-7 display the cyclic voltammetry behaviour for several lead-silver metal mixtures of increasing lead content respectively. At the lowest lead content the CV behaviour corresponds to that of the individual metal components with the peak centred at ~-0.68 V(SCE) being attributed to the Pb/PbO reversible potential, while the rest of the peaks are closely related to pure silver with the additional enhancement of the $Ag \rightarrow Ag_2O$ peak centred at +0.38 V(SCE), compare Fig. 4 and 1. Increasing lead content results in a broadening of all the silver-silver oxide peaks and eventually to a voltammogram bearing little resemblance to silver, see Fig. 7. Clearly, these results demonstrate a modification of the redox behaviour of silver with increasing lead content.

The rotating ring disc currents for O_2 reduction of some of these mixtures are presented in Fig. 8-9. Figure 10 compares the oxygen reduction currents for a sputtered silver metal film (curve 1), a sputtered platinum metal film (curve 2) and a silver-lead mixture with Pb/Ag~2.4. The mass transfer corrected Tafel plots constructed from this data for these electrodes, shown in Fig. 11, clearly demonstrate the kinetic improvement of this metal mixture over pure silver and platinum. The galvanostatically obtained low current density plots of Fig. 12, for pure silver (curve 1) and a series of lead-silver mixtures also show a significantly lower overpotential for this metal composition of Pb/Ag~2.4 (curve 5). That O_2 reduction is the reaction taking place was confirmed by stopping the flow of O_2 and saturating the solution with N_2 which was accompanied by the electrode potential shifting in the negative direction towards the H_2/H^+ potential.

There are several possible explanations for the improvement in O_2 reduction kinetics of the lead-silver mixtures over the pure silver films. First, the presence of both silver and lead at the surface may be giving rise to O_2 adsorption different than that on pure silver, resulting in increased dissociative adsorption of O_2 . Such a mechanism has been proposed to explain in part the vast improvements in oxygen reduction kinetics on gold and platinum in the presence of underpotentially deposited lead and bismuth. Secondly, the mixed and highly defective oxide at the surface may possess similar properties to those of the mixed oxide pyrochlores which exhibit excellent O_2 reduction kinetics, ie high surface anion mobilities and accessible metal redox states in the vicinity of the reversible O_2 potential. Another possibility (or contributing factor) is that the lead-silver mixture is a more active peroxide decomposition catalyst than silver. This is quite reasonable since several oxides of lead are known to be highly efficient peroxide decomposition catalysts. The result that some of the lead-silver mixtures showed negligible ring currents in films with the higher lead content supports this tends to support this view. Finally, the apparent modification of the silver/silver

oxide redox behaviour accompanied by the substantial improvement in O_2 reduction kinetics suggests the existence of a correlation.

4. SUMMARY AND CONCLUSIONS

Several atomically sputtered lead-silver mixtures reproducibly display higher activity for oxygen reduction in alkaline media than pure sputtered silver. This improvement is observed over a wide composition range up to a surface metal ratio of approximately Pb/Ag 2.4. The relative stability and reproducibility of both the disc currents in oxygen and the cyclic voltammograms in nitrogen saturated solutions indicates the absence of significant preferential dissolution of either of the metal components. The cyclic voltammetry behaviour shows that, for low lead content the voltammograms are a superposition of those for lead and silver while at high lead concentrations the CV behaviour is no longer a superposition of the two metals. The accompanying improvement in O_2 reduction kinetics suggests that there exists a correlation between the modification in redox behaviour of the silver/silver oxide system and the latter improvement. A change in mechanism of O_2 reduction is indicated by the apparent absence of solution free peroxide on mixtures with high lead concentrations.

5. FUTURE WORK

The results of this study suggest several lines of investigation should be actively and simultaneously pursued. First, a more detailed understanding of the source of the improvement of some of the lead-silver mixtures over the pure silver is required. Secondly, as a mixed oxide is clearly present on the sputtered metal mixtures after exposure to air, it seems obvious that deliberate preparation of the reactively sputter deposited mixed metal oxide and characterization of its electrocatalytic properties is necessary. Such a procedure gives one greater control over the oxide properties and hence greater reproducibility in addition to providing a useful comparison to the electrochemically generated mixed oxide. Our previous studies of metal oxides clearly supports this point of view. Thirdly, and perhaps most important, studies should be extended to other binary systems with silver where the other metal component is expected to behave similarly to lead. Examples are bismuth, neodynium, samarium and lanthanum, to mention a few.

These results and others obtained in this program (results unpublished) clearly demonstrate the utility and power of atomic sputtering as a synthetic technique for the fabrication of new materials. While the emphasis in this program is on developing new materials as O_2 reduction catalysts, one could just as easily be applying this technique to the development of new high temperature superconductors, new semi-conductors photovoltaic materials and new corrosion resistant materials, just to mention a few.

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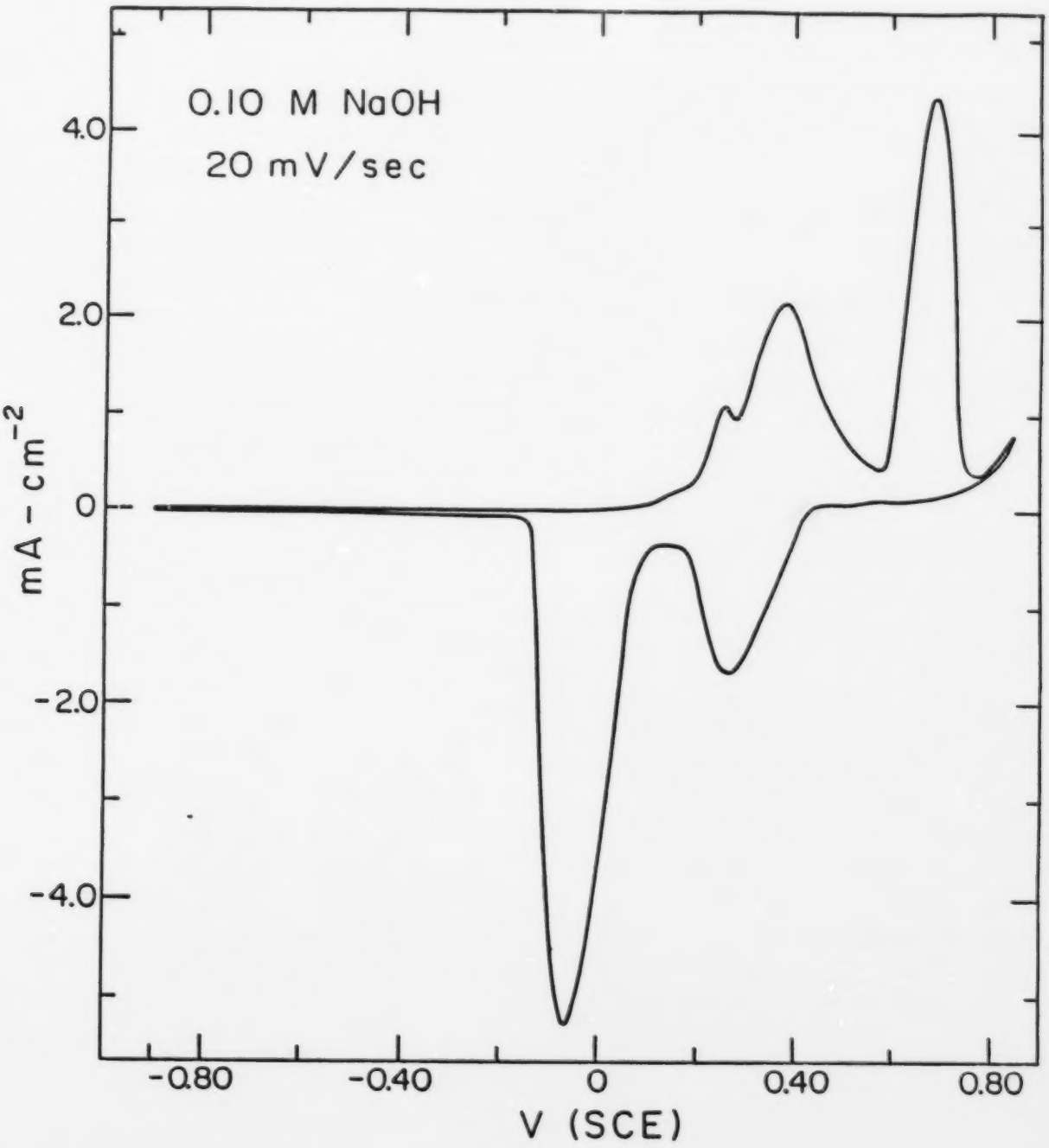

FIGURE 1

Cyclic voltammogram of atomically sputtered silver metal in nitrogen saturated 0.10 M NaOH

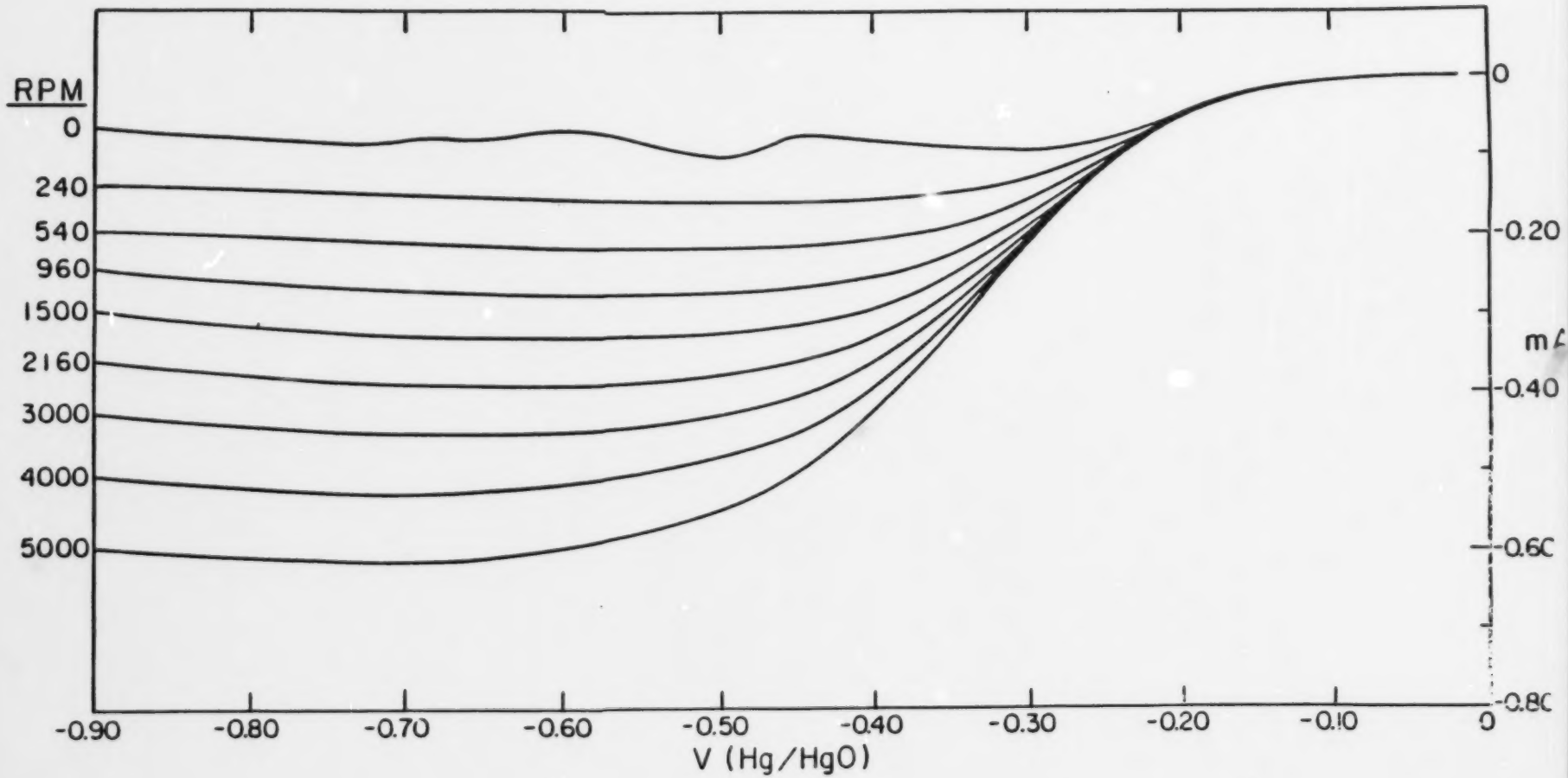

FIGURE 2

Rotating disc currents in O_2 saturated 1.0 M KOH of atomically sputtered silver film, deposited at a substrate temperature of 150°C.

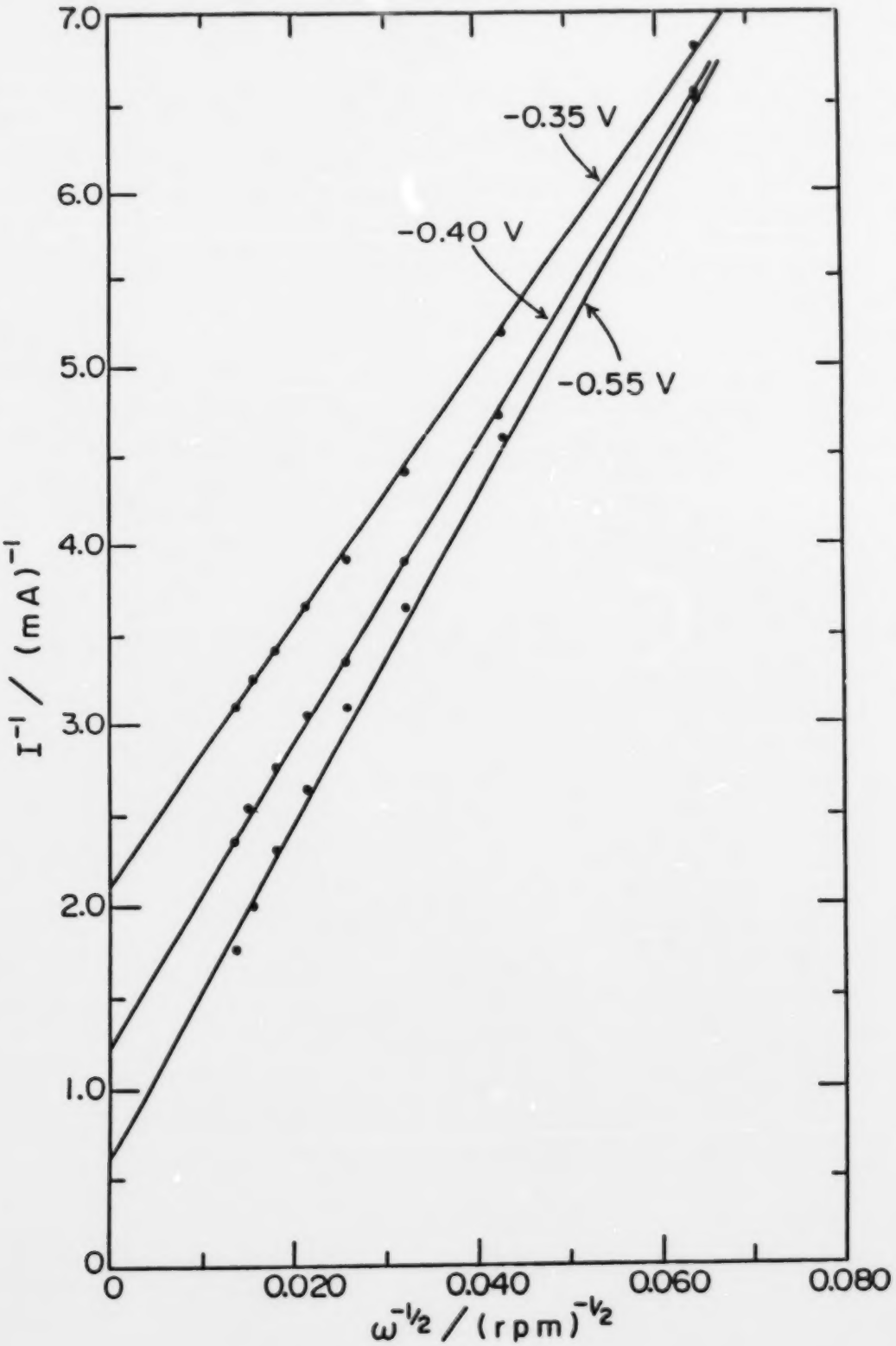

FIGURE 3

Plots of I^{-1} vs $\omega^{-\frac{1}{2}}$ for sputtered silver metal at several potentials, from the data of Fig. 2.

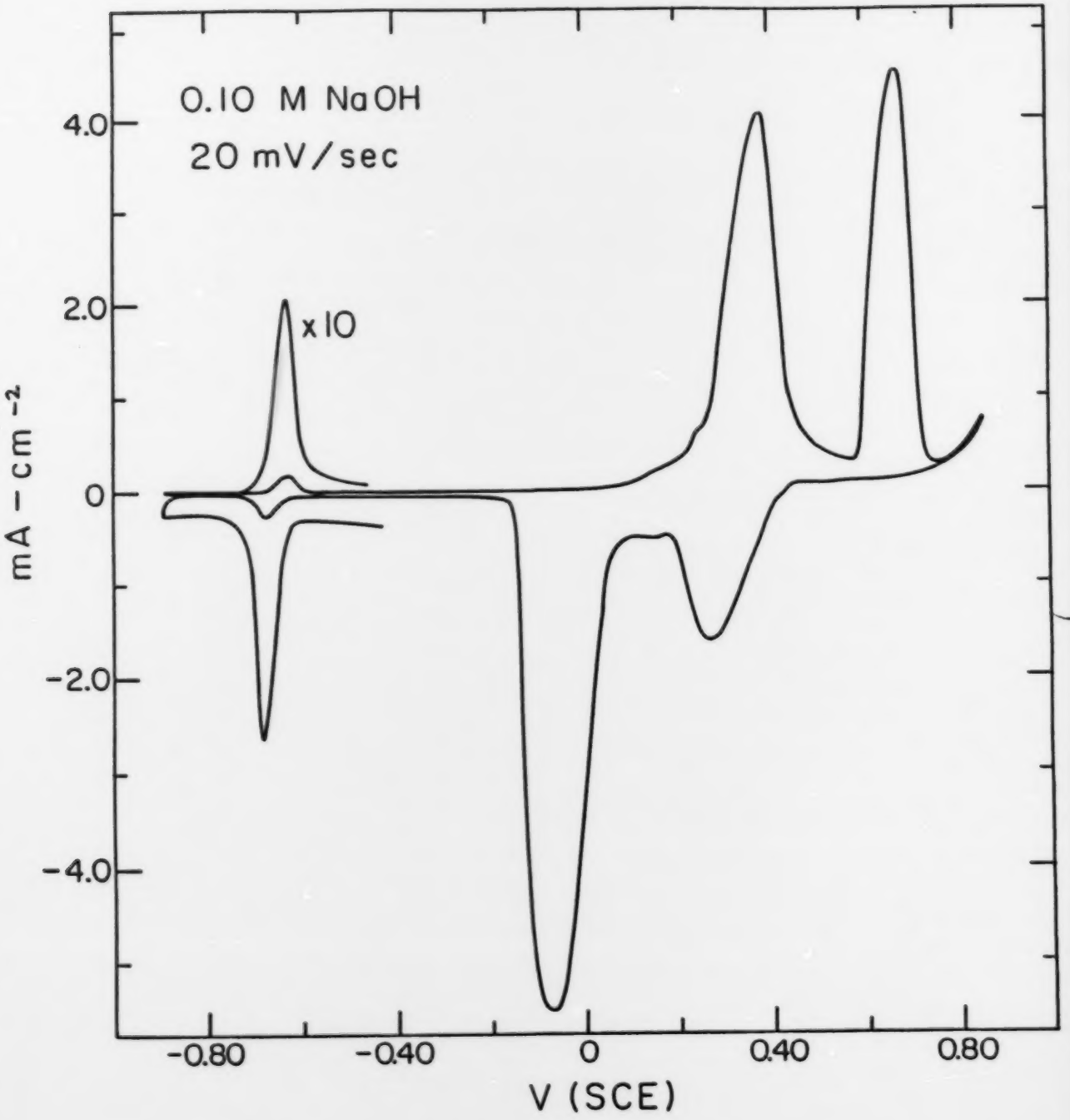

FIGURE 4

Cyclic voltammogram of lead-silver mixture in N_2 saturated 0.10 M NaOH with Pb/Ag ~ 1.2.

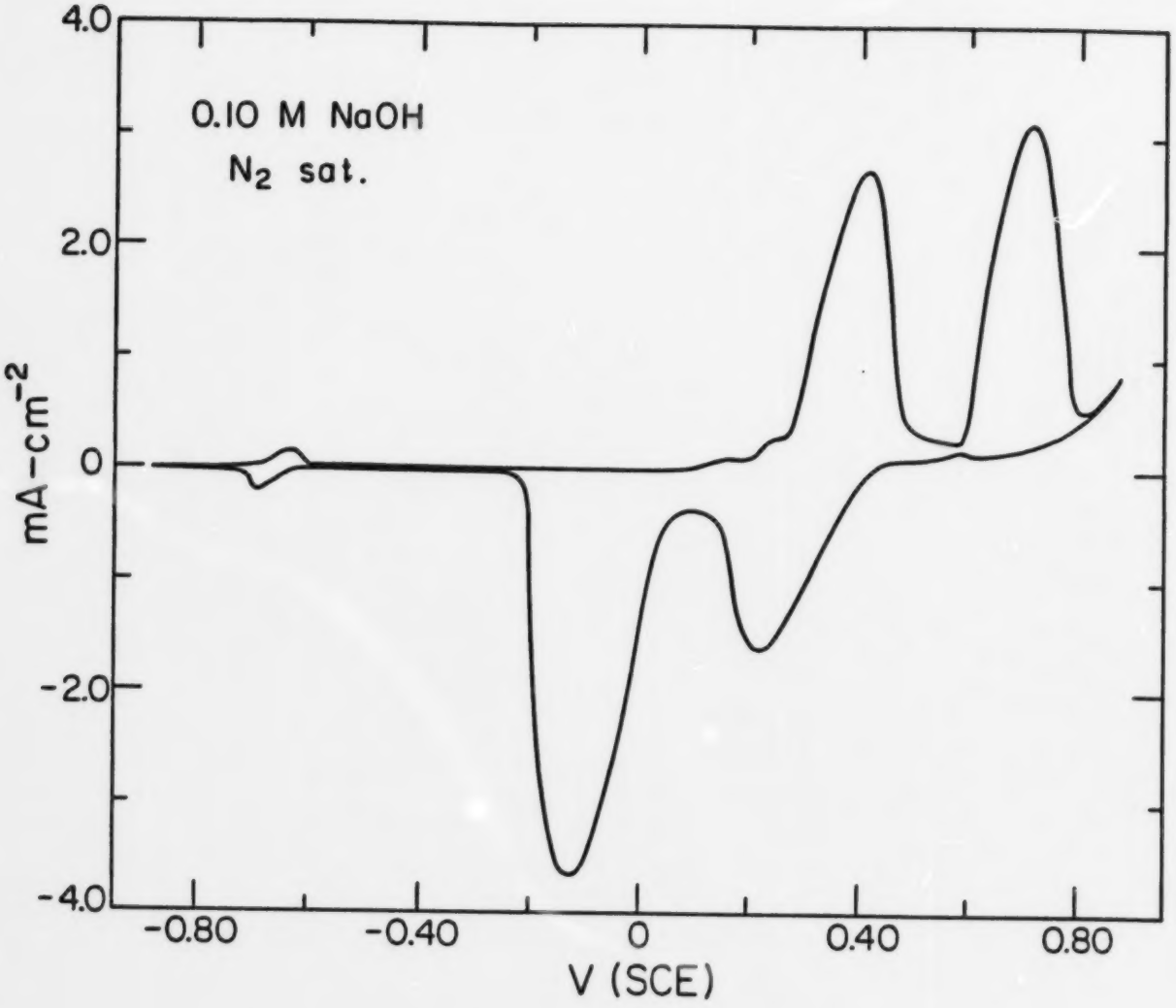

FIGURE 5

Cyclic voltammogram of lead-silver mixture in N_2 saturated 0.10 M NaOH with Pb/Ag ~ 1.5.

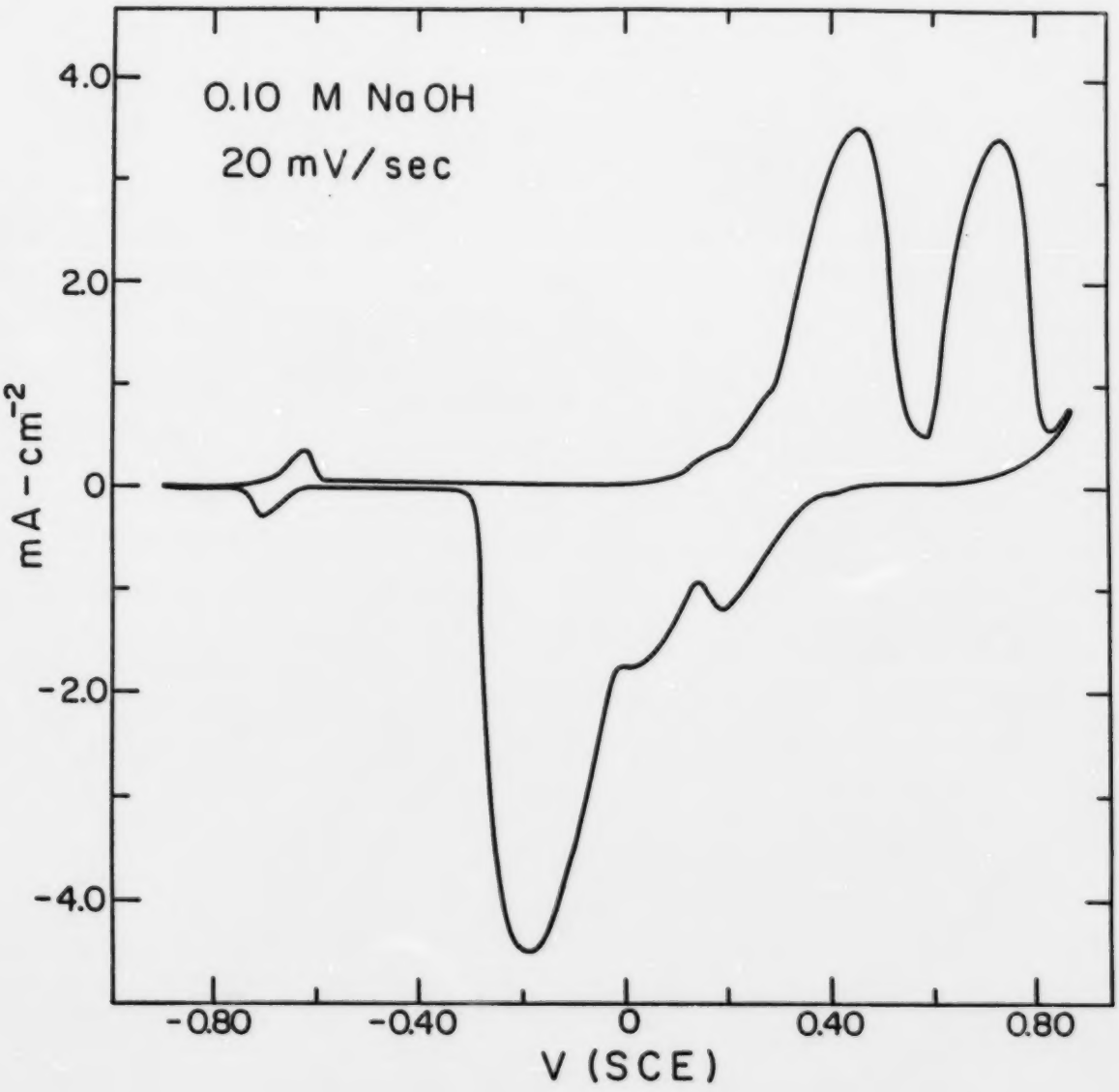

FIGURE 6

Cyclic voltammogram of lead-silver mixture in N_2 saturated 0.10 M NaOH with Pb/Ag ~ 1.9.

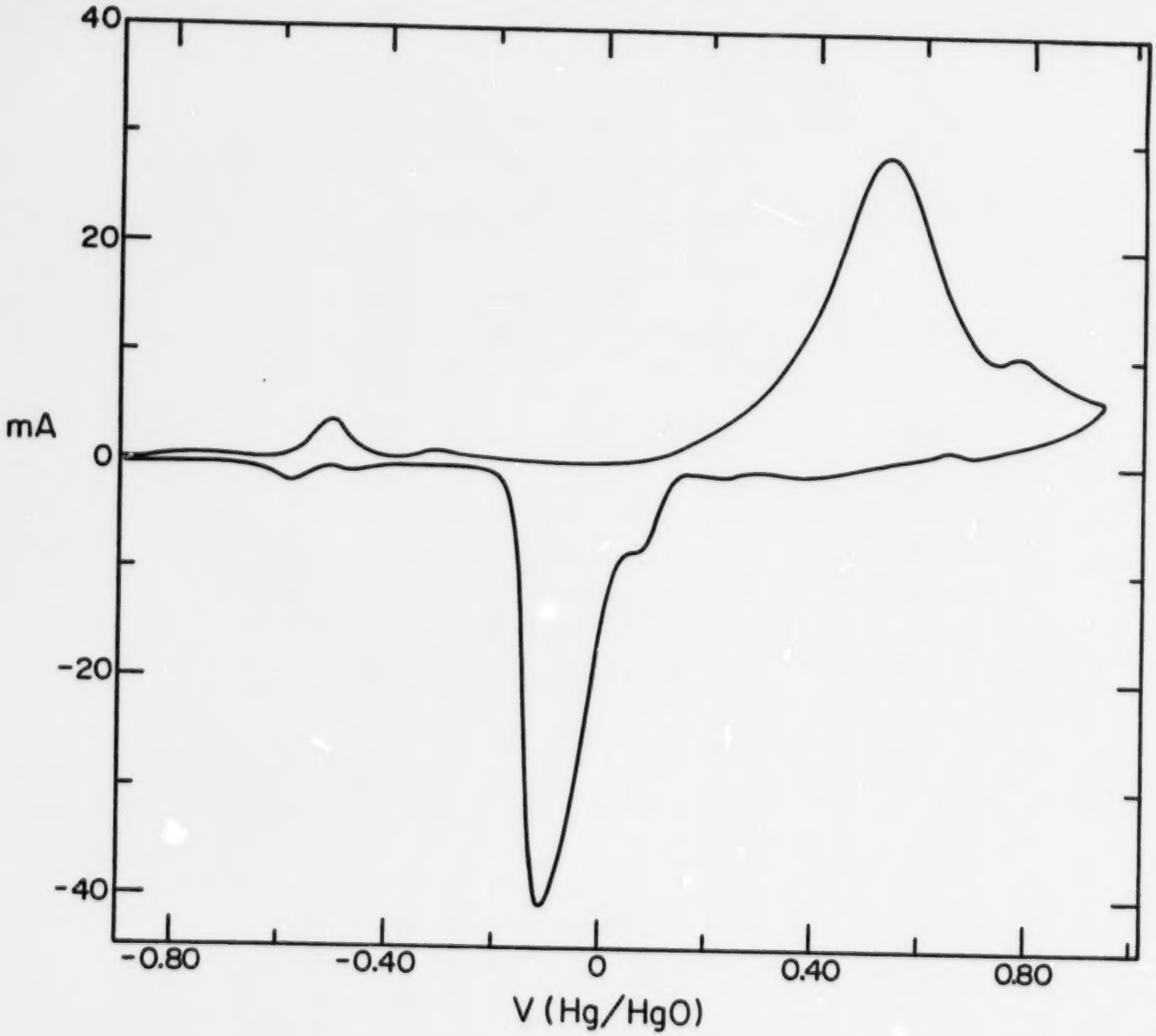

FIGURE 7

Cyclic voltammogram of lead-silver mixture in N_2 saturated 0.10 M NaOH with Pb/Ag ~ 2.4.

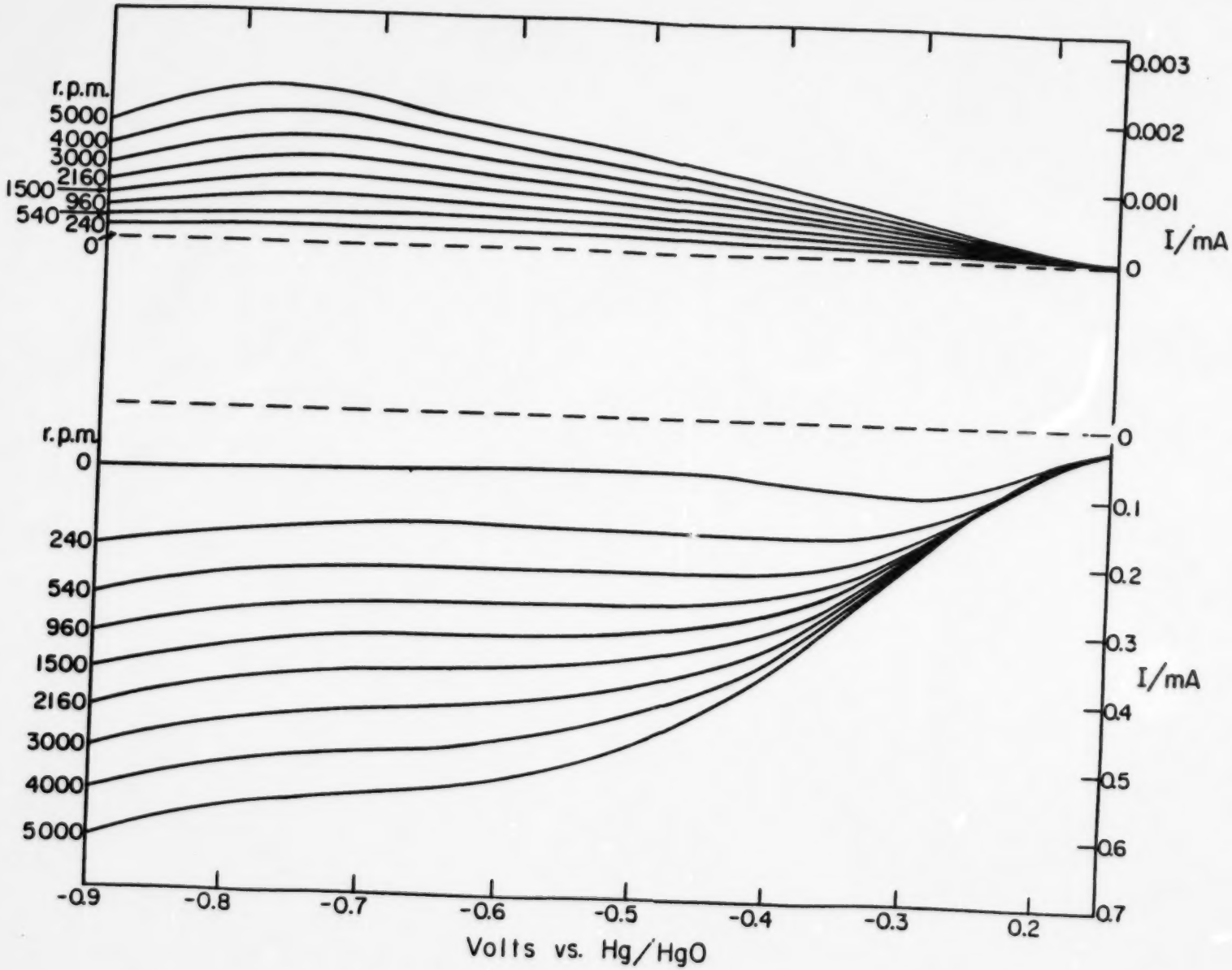

FIGURE 8

Rotating ring-disc currents for O_2 reduction in 0.10 M KOH of lead-silver mixture of Fig.4, with a surface metal ratio of Pb/Ag ~ 1.2.

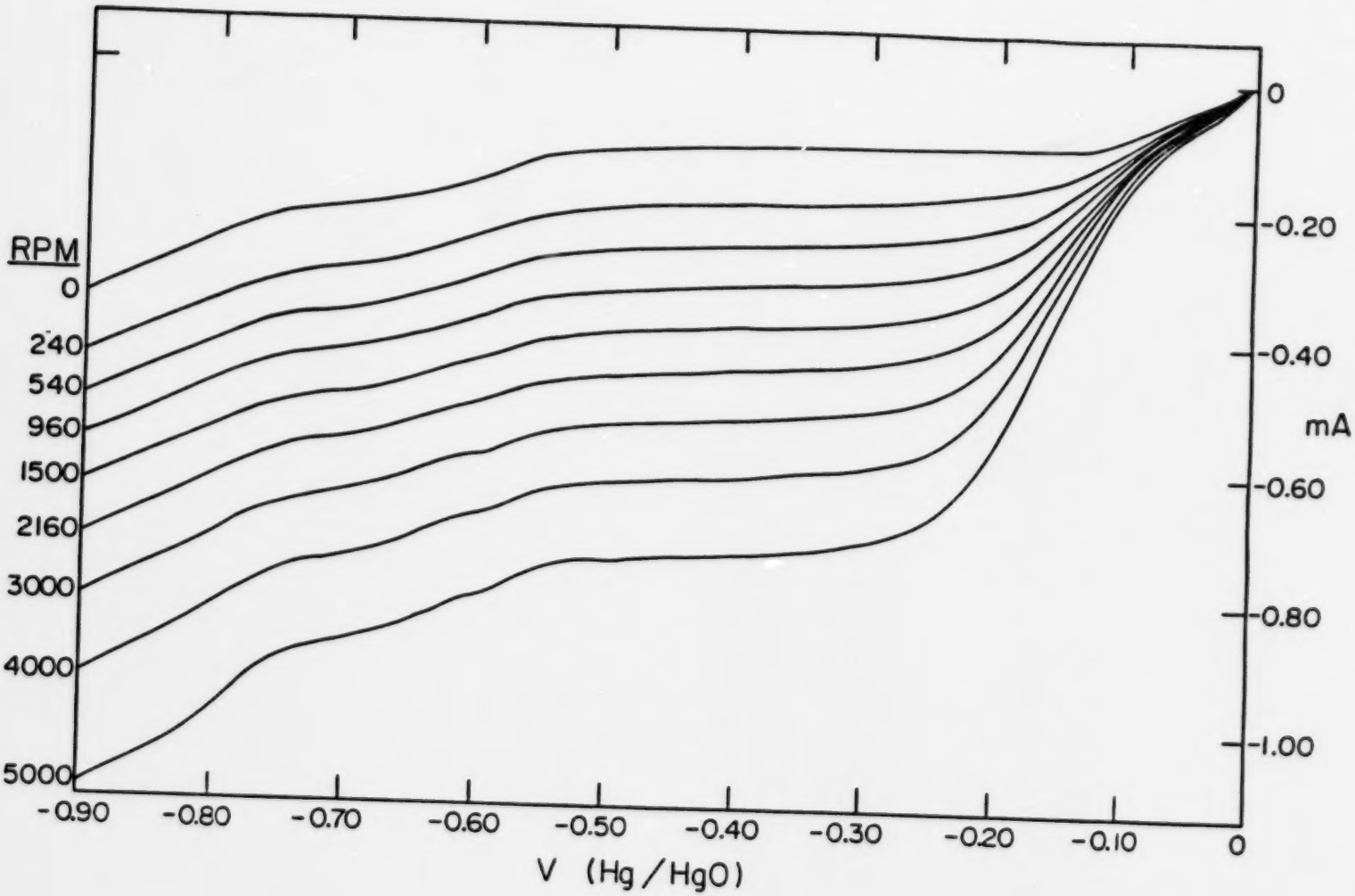

FIGURE 9

Rotating ring-disc currents for O_2 reduction in 1.0 M KOH of lead-silver mixture of Fig. 7 with a surface metal ratio of Pb/Ag ~ 2.4.

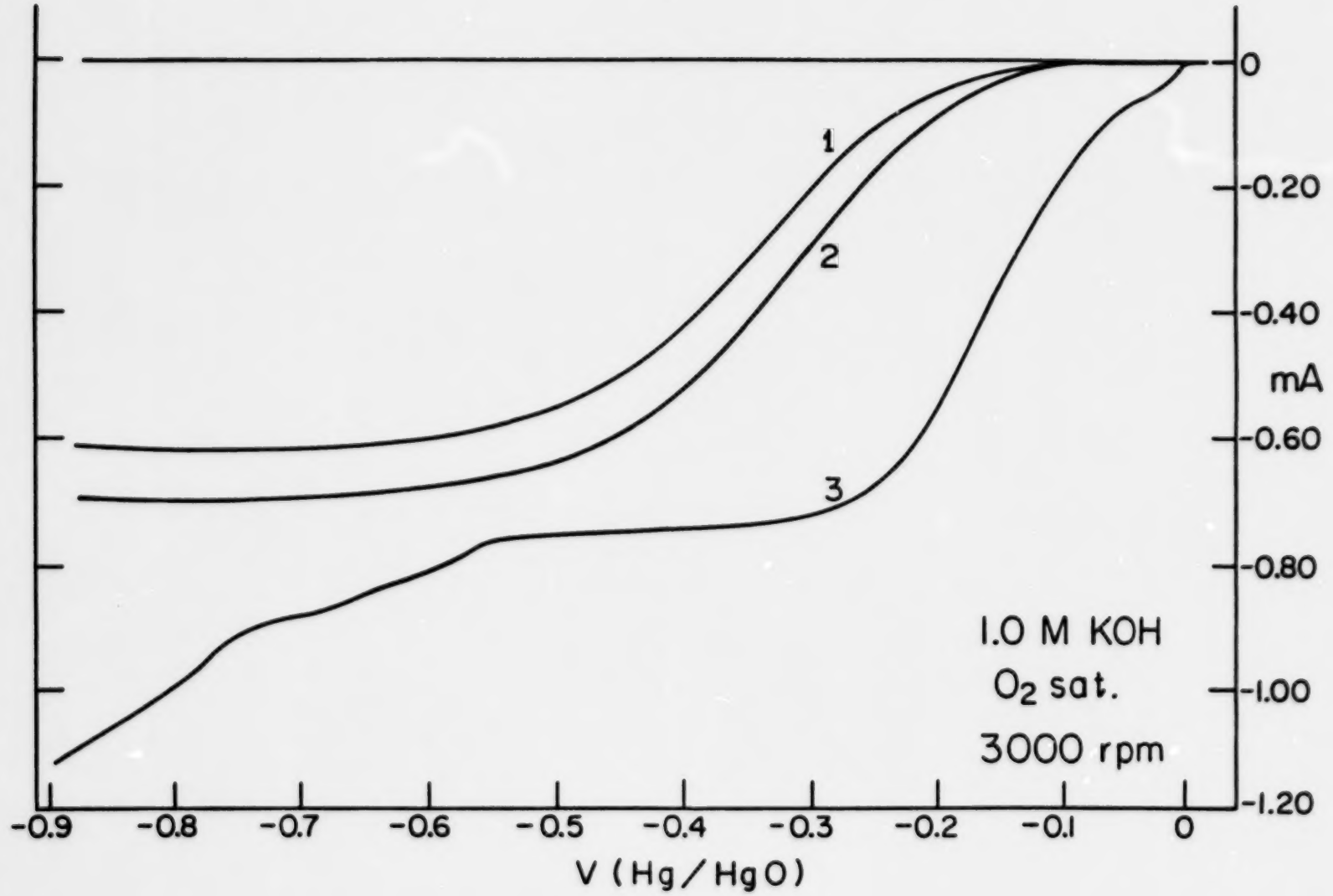

FIGURE 10

Comparison of O_2 reduction disc currents on 1-sputtered silver metal, 2-sputtered platinum metal and 3-sputtered silver-lead metal mixture with a surface ratio of Pb/Ag 2.4 at 3000 rpm in O_2 saturated 1.0 M KOH, all deposited onto discs of area 0.196 cm^2

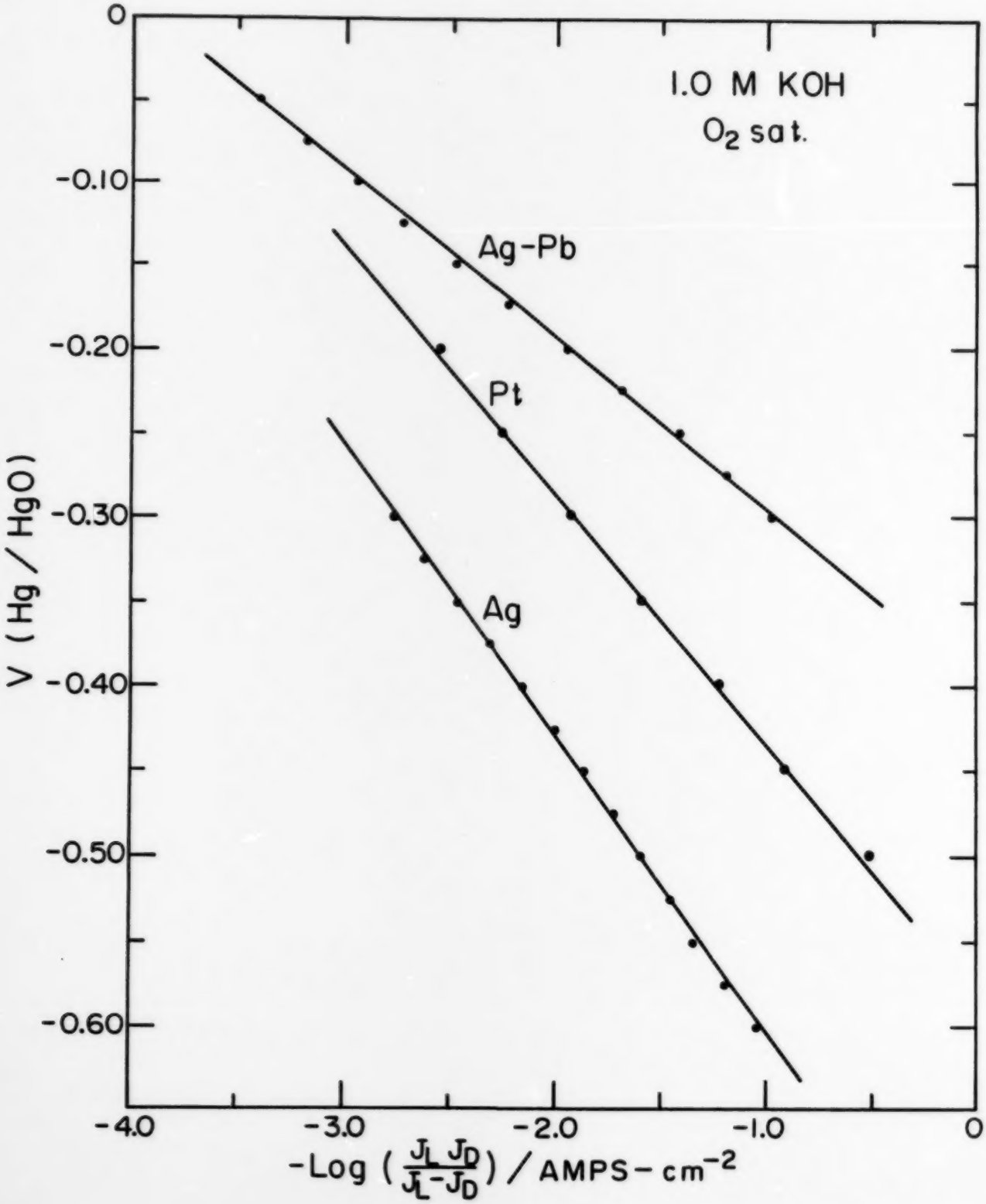

FIGURE 11

Mass transfer corrected Tafel plots of 0_2 reduction on the three electrodes of Figure 10

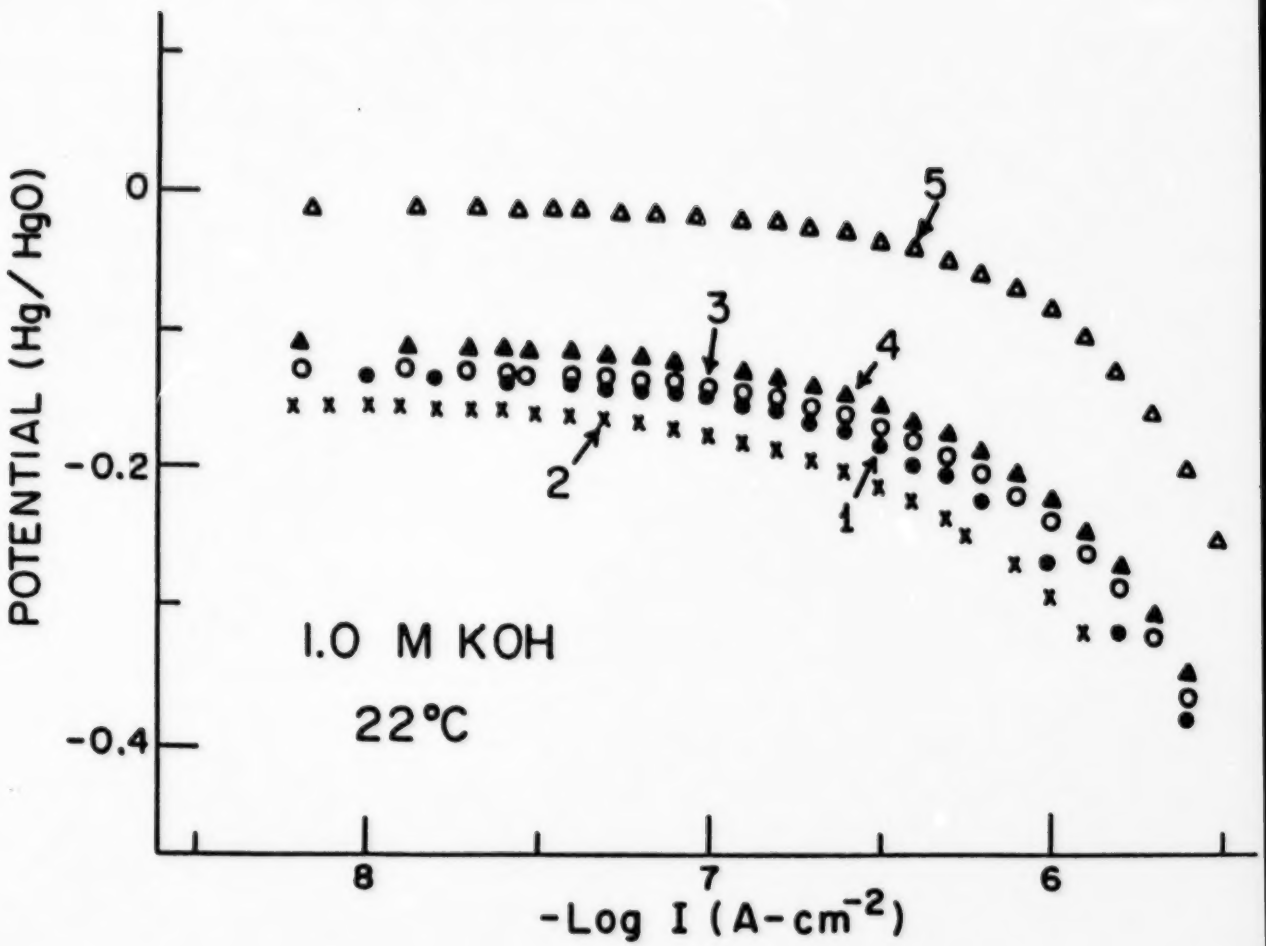

FIGURE 12

Low current density polarization plots obtained galvanostatically on pure silver and three lead-silver mixtures, 1: sputtered silver metal, 2: lead-silver mixture with Pb/Ag ~3.5; 3,4: two different samples with surface metal ratios of Pb/Ag ~ 1.9; 5: lead-silver mixture with Pb/Ag ~ 2.4.